

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08G 83/00	A1	(11) International Publication Number: WO 98/50453 (43) International Publication Date: 12 November 1998 (12.11.98)
(21) International Application Number: PCT/GB98/01276 (22) International Filing Date: 1 May 1998 (01.05.98) (30) Priority Data: 9709045.0 2 May 1997 (02.05.97) GB (71) Applicant (for all designated States except US): COUR- TAULDS COATINGS (HOLDINGS) LIMITED [GB/GB]; 50 George Street, London W1A 2BB (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): DAVIS, Nicola, Jane [GB/GB]; 26 Dorothy Powell Way, Walsgrave, Coventry CV2 2TN (GB). RANNARD, Steven, Paul [GB/GB]; 26 Oak Road, Tiddington, Stratford-Upon-Avon, Warwick- shire CV37 7BU (GB). (74) Agent: HALE, Stephen, Geoffrey; J.Y. & G.W. Johnson, Kingsbourne House, 229-231 High Holborn, London WC1V 7DP (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: POLYMERS AND THEIR PREPARATION <div style="text-align: center;"> </div> (57) Abstract <p>Hyperbranched polymers containing linkages selected from urea, urethane, carbonate, ester and amine linkages are described. A hyperbranched polymer is prepared by reacting a polyfunctional compound having three reactive functional groups (B) in substantially equimolar quantities with a reagent which reacts rapidly with group (B) to form a group (A) which reacts more slowly with group (B), or by the polymerisation of a compound containing a single group (A) of one chemical type and at least two groups (B) of a different chemical type which is reactive with (A), either (A) or (B) being a group of formula (I) where Q represents O or S and X represents -O-, -S-, -NH- or a direct bond.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

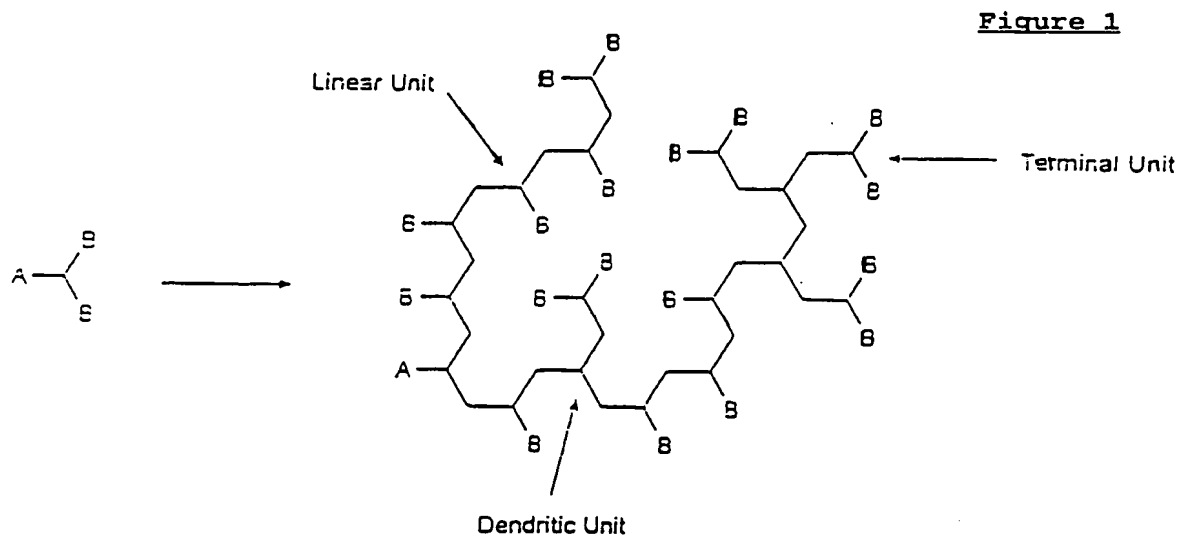
AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

- 1 -

Polymers and their PreparationField of the invention

This invention relates to highly branched polymers known as hyperbranched polymers and to reactions for their preparation.

Hyperbranched polymers are generally prepared by the polymerisation in a single reaction of a compound (monomer) containing a single group (A) of one chemical type and at least two groups (B) of a different chemical type which is reactive with (A). Such a monomer will react as shown in Figure 1 below to form a branched polymer containing one group (A) and (x+1) groups (B) if x monomer molecules have reacted together.



The polymerisation of an AB_2 monomer leads to a complex mixture of products containing both linear and dendritic regions. Three types of subunit are found within a hyperbranched polymer formed from an AB_2 monomer. These differ in the number of B functionalities which have reacted. If both have reacted a dendritic unit is formed, if

- 2 -

only one has reacted a linear unit is formed and if no B groups have reacted a terminal unit is formed.

The ratio of these units can be used to determine the degree of branching of the polymer.

5 Degree of Branching =

$$\frac{\text{Number of Dendritic Units} + \text{Number of Terminal Units}}{\text{Total number of Units}}$$

The degree of branching for an ideal dendrimer is equal to 1. A linear polymer has a degree of branching of approximately 0. A hyperbranched polymer has a structure intermediate between a dendrimer and a linear polymer and can in theory have a degree of branching between 0 and 1 but generally is only considered as a hyperbranched polymer when the degree of branching is greater than 0.4 as described in
15 US-A-5514764.

Background art

Hyperbranched polyesters are described for example in US-A-5418301, US-A-5514764 and WO-A-96/12754. Hyperbranched polycarbonates are described by D.H. Bolton and K. L. Wooley
20 in *Macromolecules* 1997, vol. 30, page 1890. Hyperbranched polyphenylenes are described by Y.H. Kim and O.W. Webster in *Macromolecules* 1992, 25, 5562. Hyperbranched polyethers are described by K. E. Uhrich, C.J. Hawker, J.M.J. Frechet and S.R. Turner in *Macromolecules*, 1992, 25, 4583. Hyperbranched
25 polyetherketones are described by F. Chu and C.J. Hawker in *Polymer Bulletin*, 1993, 30, 265. Hyperbranched polyurethanes are described by A. Kumar and S. Ramakrishnan in *J. Chem. Soc. Commun.* 1993, 18, 1453 and by R. Spindler and J.M.J. Frechet in *Macromolecules*, 1993, 26, 4809. Hyperbranched
30 poly(ester-amide)s are described by H.R. Kricheldorf and G. Lohden in *Macromol. Chem. Phys.*, 1995, 196, 1839.

Hyperbranched polymers have wide industrial potential for use in high-solids coatings and sealants, as reactive plasticisers and as substrates for binding biological

- 3 -

reagents such as enzymes or antigens owing to their characteristics such as lower viscosity when molten or in solution when compared to their linear analogues, higher solubility than their linear analogues and high chemical reactivity (large number of reactive chain ends). There is a need for further reactions capable of producing hyperbranched polymers without premature crosslinking and without needing protection and deprotection of reactive groups.

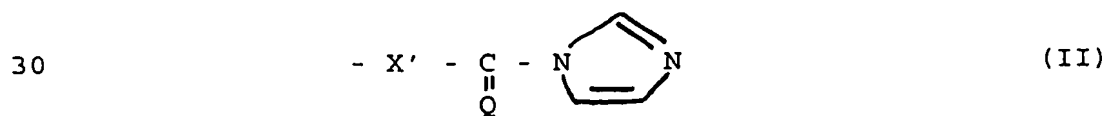
10 Disclosure of the invention

A process according to one aspect of the present invention for the preparation of a hyperbranched polymer by the polymerisation of a compound containing a single group (A) of one chemical type and at least two groups (B) of a different chemical type which is reactive with (A) is characterised in that the single group (A) is a group of the formula:



20 where Q represents O or S and X represents -O-, -S-, -NH- or a direct bond, the group being linked to the remainder of the compound through a carbon atom.

According to another aspect of the invention, a process for the preparation of a hyperbranched polymer by the polymerisation of a compound containing a single group (A) of one chemical type and at least two groups (B) of a different chemical type which is reactive with (A) is characterised in that either the group (A) or the group (B) is a group of the formula:-



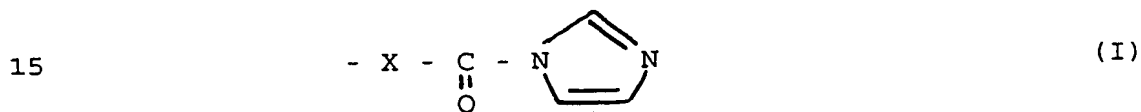
where Q represents O or S and X' represents -NH- or a direct

- 4 -

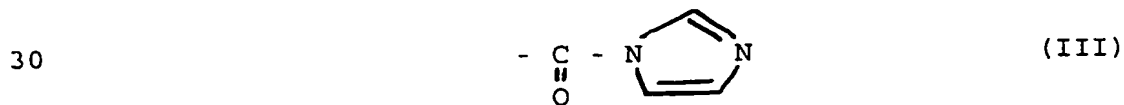
bond, the group being linked to the remainder of the compound through a carbon atom.

When the groups (B) are 1-imidazole carboxamides and the group (A) is a secondary amine group hyperbranched 5 polyureas are formed. When the groups (B) or the group (A) are or is an imidazolidine linked to the remainder of the molecule through a carbon atom and the group (A) or the groups (B) respectively is or are a hydroxyl group hyperbranched polyesters are formed. When the groups (B) or 10 the group (A) are or is a 1-imidazole carboxamide and the group (A) or the groups (B) respectively is or are primary or secondary alcohol groups hyperbranched polyurethanes are formed.

The imidazolidine group of the formula:



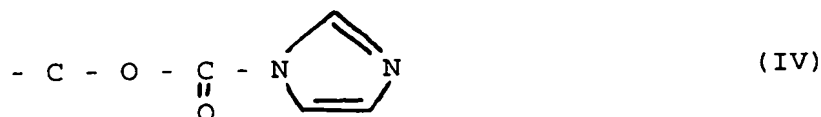
can in general be produced by reaction of a compound or polymer containing hydroxyl, thiol, amine or carboxylic acid groups with carbonyl diimidazole or thiocarbonyl 20 diimidazole. The imidazole ring can be substituted or can be fused to a benzene ring, leading to a substituted imidazole ring in the group of formula (I), but this is not preferred. The preferred reagent is carbonyl diimidazole. Alcohol groups, thiol groups, primary amino groups and carboxylic 25 acid groups react with carbonyl diimidazole to form an imidazolidine in which an active hydrogen atom of the alcohol, thiol and/or amino groups, and/or the whole carboxylic acid group, is replaced by a carbonyl imidazole group of the formula:



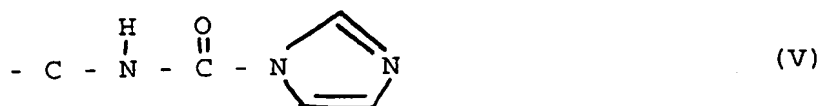
The term "imidazolidine" is used in this specification to

- 5 -

describe a 1-imidazole carboxyl ester of an alcohol having the structure:



5 or a 1-imidazole carboxamide having the structure:



as well as an imidazolidine having the structure:



The imidazolidine group can be prepared in alternative ways, although preparation from carbonyl diimidazole is most convenient. 1-Imidazole carboxyl esters can be prepared by reaction of a chloroformate with imidazole or by reaction of
15 the carbonyl chloride of imidazole with an alcohol. 1-Imidazole carboxamides can be prepared by reaction of a carbamoyl chloride with imidazole or by reaction of the carbonyl chloride of imidazole with an amine. 1-Imidazole carbonyl compounds can be prepared by reaction of an acyl
20 chloride with imidazole.

The imidazolidine group can in general be the single A group in an AB₂ monomer, forming on polymerisation a hyperbranched polymer having terminal groups B which are the functional groups reactive with the imidazolidine, or the
25 groups B in an AB₂ monomer can be imidazolidine groups, forming a hyperbranched polymer having terminal imidazolidine groups. These terminal imidazolidine groups can be reacted in a further step to convert them to different groups if desired.

- 6 -

The group reacted with carbonyl diimidazole to form the group (A) or (B) of an AB_n monomer is preferably a carboxylic acid group or primary amine group. Carboxylic acid groups react with carbonyl diimidazole to replace one imidazole ring to form an imidazolide readily at ambient temperature without need for a catalyst, with little tendency towards further reaction to replace the remaining imidazole ring. Primary amines are capable of reacting with carbonyl diimidazole at room temperature without need for a catalyst to replace both imidazole rings, forming a urea linkage, if the primary amine is present in stoichiometric excess, but if the reagents are used in stoichiometrically equivalent amounts or if the carbonyl diimidazole is used in excess, the predominant reaction is to replace only one of the imidazole rings of the carbonyl diimidazole.

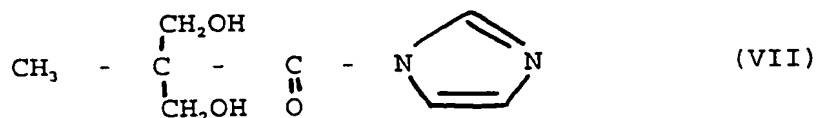
According to another aspect of the invention, a process for the preparation of a hyperbranched polymer by the polymerisation of a compound containing a single group (A) of one chemical type and at least two groups (B) of a different chemical type which is reactive with (A) is characterised in that a precursor compound, containing either a single group (A') of one chemical type reactive with carbonyl diimidazole and at least two groups (B) of a different chemical type from A' which is less reactive than A' with carbonyl diimidazole or at least two groups (B') of one chemical type reactive with carbonyl diimidazole and a single group (A) of a different chemical type from B' which is less reactive than B' with carbonyl diimidazole, is reacted with carbonyl diimidazole under conditions such that only the group A' or the groups B' react with the carbonyl diimidazole to form imidazolide groups, and the resulting compound containing imidazolide groups is polymerised under more vigorous reaction conditions to form the hyperbranched polymer.

Alcohol groups will react readily with carbonyl diimidazole in the presence of a basic catalyst or on

- 7 -

heating but only very slowly at room temperature without catalyst. Primary alcohol groups can react to replace both imidazole rings, forming a carbonate linkage, and are preferably not used in stoichiometric excess. Secondary and
5 tertiary alcohol groups generally show little tendency to further reaction to replace the remaining imidazole ring.

This requirement for a catalyst or for heating can be used in a convenient method for preparing an AB₂ monomer and then polymerising it to form a hyperbranched polymer
10 according to the invention. For example, a precursor compound containing one carboxylic acid group (A') and two hydroxyl groups, such as 2,2-bis(hydroxymethyl)propionic acid or 3,5-dihydroxybenzoic acid or the N,N-bis(2-hydroxyethyl) monoamide of adipic acid, can be reacted with
15 carbonyl diimidazole at room temperature without catalyst to form an imidazolide such as

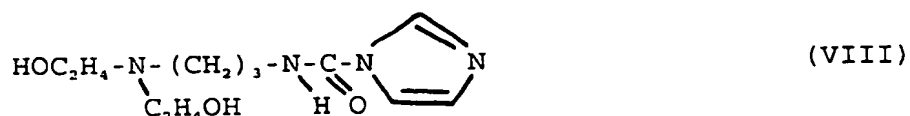


20 The hydroxyl group can for example be a primary alcohol group or an unhindered secondary alcohol group such as a -CHOHCH₃ group or a phenol group when the carboxylic acid is aliphatic; almost all primary and secondary alcohol and phenol groups are suitable if the carboxylic acid is
25 aromatic. This compound containing one imidazolide group and two alcohol groups can be used as an AB₂ monomer. It is substantially stable at ambient temperature (up to 30°C) in the absence of catalyst. Under more vigorous conditions, for example when heated to at least 50°C, preferably 50-120°C,
30 intermolecular reaction takes place between an alcohol group and an imidazolide group, forming a larger molecule containing one imidazolide group together with an ester linkage and alcohol groups and eventually a hyperbranched polyester having terminal hydroxyl groups. Alternatively,
35 the imidazolide can be polymerised by addition of a basic catalyst, for example KOH, NaOH, a quaternary ammonium

- 8 -

hydroxide or a strongly basic amine such as diazabicycloundecene.

Similarly, a precursor compound containing one primary amine group (A') and two primary or secondary alcohol groups, such as N-(3-aminopropyl) diethanolamine, can be reacted with a substantially equimolar amount of carbonyl diimidazole to form an imidazolidine such as



10 This is stable at ambient temperature in the absence of catalyst and can be used as an AB₂ monomer which is activated by heating or by a basic catalyst, forming a hyperbranched polyurethane having terminal hydroxyl groups.

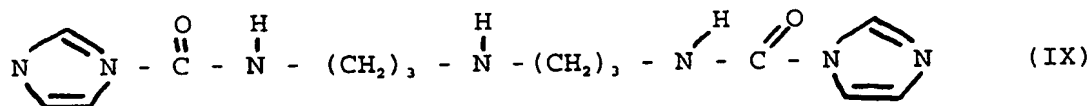
Alternatively, the precursor compound can contain two
15 or more carboxylic groups (B') and a single hydroxyl group, for example 5-hydroxyisophthalic acid, or two or more primary amine groups (B') and a single primary or secondary alcohol group, for example N,N'-bis(3-aminopropyl)ethanolamine. Such a precursor compound can be
20 reacted with carbonyl diimidazole to produce a compound containing a single hydroxyl group and two or more imidazolidine groups. In the case of the diamine, a substantially stoichiometric amount of carbonyl diimidazole (2 moles per mole diamine) must be used. This compound can
25 be polymerised by heating or addition of basic catalyst to form a hyperbranched polymer having terminal imidazolidine groups.

It is generally preferred that compounds having functional groups on adjacent carbon atoms, such as glycerol
30 or 2-amino-1,3-propanediol or diethylene triamine are not reacted with carbonyl diimidazole in the process of the invention, since such compounds tend to undergo a cyclisation reaction forming a cyclic carbonate, urethane or

- 9 -

urea which is not useful in preparing hyperbranched polymers.

Hyperbranched polyureas (in which all or most of the chemical linkages in the polymer are urea linkages) can be formed by the reaction of a diprimary secondary triamine as precursor compound in which the primary amine groups act as reactive groups B', for example dipropylene triamine, bis(hexamethylene) triamine or N-(2-aminoethyl)-propane-1,3-diamine, with carbonyl diimidazole at low temperature, preferably 0°C or below, followed by heating to ambient temperature (e.g. 20 or 25°C) or above to polymerise the resulting AB₂ monomer. Secondary amine groups react with carbonyl diimidazole at room temperature or above but the imidazolidine formed is rather stable and does not readily react with any alcohol or amine groups. Secondary amine groups react readily with imidazolidine groups formed from primary amines, aromatic acids or primary alcohols. Primary amine groups react more rapidly with carbonyl diimidazole than do secondary amine groups. Thus, if dipropylene triamine is reacted with carbonyl diimidazole at 0°C the preponderant product is



When this is polymerised, the hyperbranched polyurea product has a plurality of terminal imidazolidine groups. Alternatively, a primary dissecondary amine can be reacted with carbonyl diimidazole to produce a compound containing one imidazolidine group and two secondary amine groups and this can be polymerised at room temperature or above to produce a hyperbranched polyurea.

Imidazolidine groups are generally reactive with amine groups and with most primary or secondary hydroxyl groups; a hyperbranched polymer having terminal imidazolidine groups can thus be used as a crosslinking agent in coating or

- 10 -

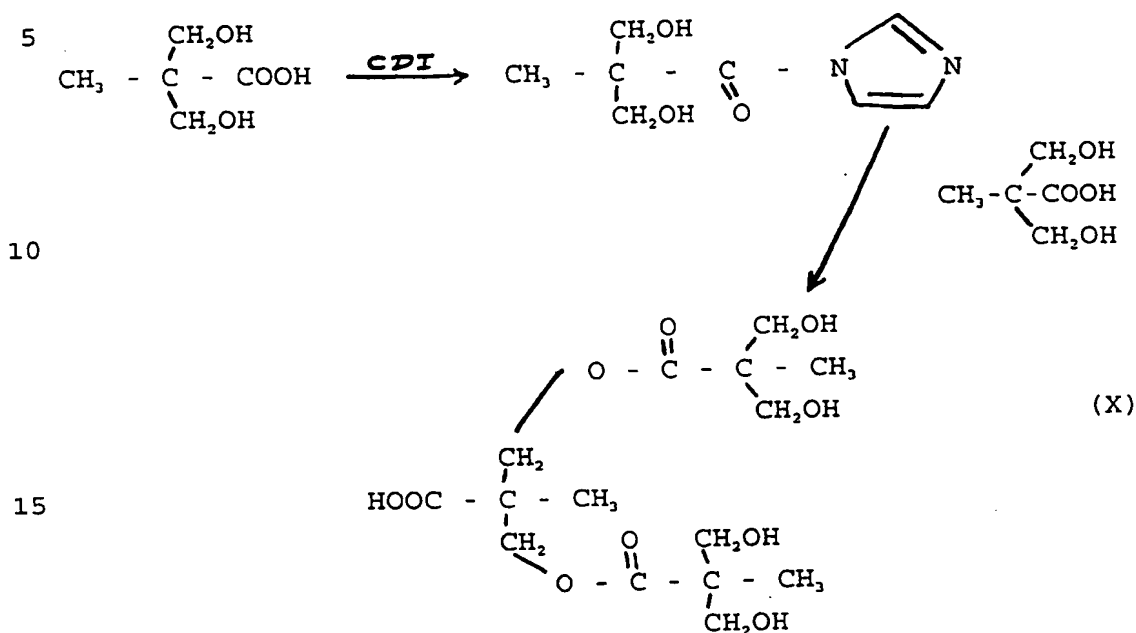
sealant compositions. Alternatively, such a hyperbranched polymer can be reacted with a monofunctional amine or primary or secondary alcohol to form a non-functional hyperbranched polymer, or it can be reacted with an amine or
5 primary or secondary alcohol containing a functional group (C) not reactive with the imidazolidine group, for example a carboxylic acid group, to produce a hyperbranched polymer having functionality (C). Mixtures of reagents, for example a mixture of a monoamine and an aminoacid, can be used to
10 form a hyperbranched polymer having a controlled number of functional groups. Alternatively, the hyperbranched polymer can be reacted with water to hydrolyse the imidazolidine group. For example, the terminal imidazolidine groups of the hyperbranched polyurea described above can be hydrolysed to
15 form terminal amine groups. Terminal imidazolidine groups derived from a carboxylic acid hydrolyse very readily to form terminal carboxylic acid groups.

Any of the above processes can be modified to increase or decrease the degree of branching of the hyperbranched
20 polymer. The degree of branching can be decreased by the incorporation of an AB monomer, which can form only linear units, with the AB₃ monomer. For example, a mixture of a dihydroxycarboxylic acid and a monohydroxycarboxylic acid such as lactic acid, gamma-hydroxybutyric acid or 2,2-
25 dimethyl-3-hydroxypropionic acid can be reacted with carbonyl diimidazole to produce a mixture of imidazolidines which act as AB₂ and AB monomers and can be polymerised by heating or by a strong base catalyst to form a branched polyester containing an increased proportion of linear
30 units.

The degree of branching can be increased by the use of an AB₄ compound having a dendritic structure as all or part of the monomer forming the hyperbranched polymer. For example, a dihydroxycarboxylic acid such as
35 bis(hydroxymethyl)propionic acid can be reacted with carbonyl diimidazole as described above and the resulting

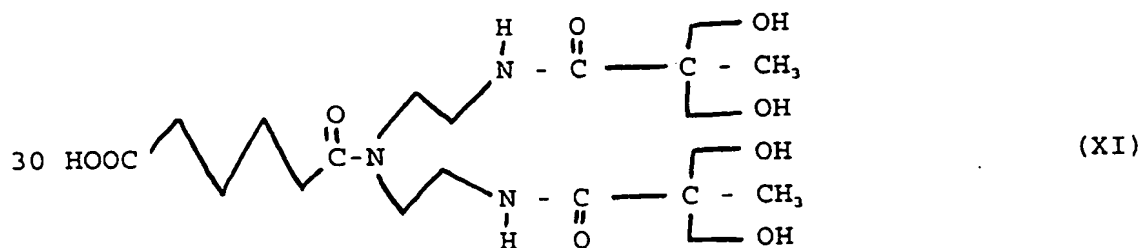
- 11 -

imidazolidine can be reacted with further dihydroxycarboxylic acid by heating or in the presence of a strong base catalyst to form a dendritic compound having one carboxylic acid group and four hydroxyl groups as shown below.



This can be reacted with carbonyl diimidazole to form an AB₄ monomer which can be polymerised to a hyperbranched polymer by heating or by a strong base catalyst.

Alternatively, the imidazolidine of a dihydroxycarboxylic acid can be reacted with a diaminocarboxylic acid such as an N,N-bis(2-aminoethyl) monoamide of a dicarboxylic acid to prepare a dendritic compound containing one carboxylic acid group and four hydroxyl groups.



- 12 -

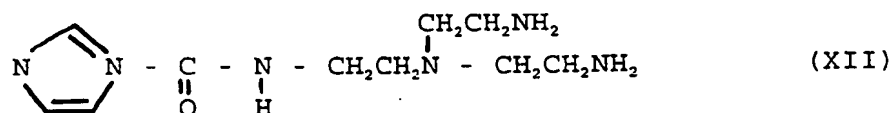
This can be reacted with carbonyl diimidazole to form an AB₄ monomer and polymerised by heating or by a strong base catalyst to form a hyperbranched polymer containing both amide and ester linkages.

5 An alternative method according to the invention for the preparation of hyperbranched copolymers is by the copolymerisation of two or more different imidazolidine compounds. Hyperbranched copolymers containing different linkages can be prepared by copolymerising two or more
10 different imidazolidines, in particular those in which the groups of formula (I) are different. For example, the imidazolidine of a dihydroxycarboxylic acid can be copolymerised with the imidazolidine of a dihydroxyamine (in which the hydroxyl groups are primary or secondary alcohol
15 groups and the amine group is a primary or secondary amine group), such as N-(3-aminopropyl) diethanolamine, to form a hyperbranched copolymer containing both ester and urethane links.

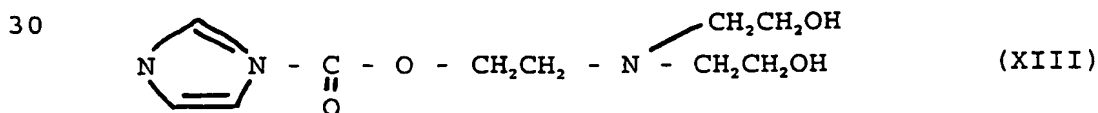
Thus, according to another aspect of the invention a
20 hyperbranched polymer formed by the polymerisation of at least one compound containing a single group (A) of one chemical type and at least two groups (B) of a different chemical type which is reactive with (A) is characterised in that the hyperbranched polymer is a copolymer containing two
25 different chemical linkages, one of said linkages being selected from urea, urethane and carbonate linkages and the other of said linkages being selected from urea, urethane, carbonate, ester and amide linkages.

Alternatively, hyperbranched copolymers containing both
30 aromatic and aliphatic groups can be produced by copolymerising two imidazolidines, one of which is an aromatic compound such as the imidazolidine of 3,5-dihydroxybenzoic acid and the other of which is an aliphatic compound such as the imidazolidine of 2,2-bis(hydroxymethyl) propionic acid.

A process according to another aspect of the invention for the preparation of a hyperbranched polymer is characterised in that a polyfunctional compound having at least three reactive functional groups (B) is reacted in substantially equimolar quantities with a reagent which reacts rapidly with group (B) to form a group (A) which reacts more slowly with group (B) than the reagent does. Examples of such reagents are carbonyl diimidazole and thiocarbonyl diimidazole, which react rapidly with primary amino groups or primary alcohol groups to form imidazolide groups which react less rapidly with the remaining primary amino or primary alcohol groups than the reagent does. The reaction with primary amine can be carried out at ambient temperature in the absence of catalyst. A strong base catalyst or elevated temperature, for example 50 to 120°C, is needed with the alcohol. An example of a suitable tri(primary amine) is tris(2-aminoethyl)amine and an example of a suitable tri(primary alcohol) is triethanolamine. The carbonyl diimidazole reacts rapidly with one primary amine group, predominantly forming the AB₂ monomer



before the subsequent slower reaction of the imidazolidine
25 group with the primary amine groups to form urea linkages
and eventually an amine-functional hyperbranched polyurea.
We believe that hyperbranched polyureas have not previously
been prepared. Similarly triethanolamine reacts rapidly to
form predominantly



before the subsequent slower reaction to form carbonate linkages and eventually a hydroxy-functional hyperbranched

- 14 -

polycarbonate.

The reagent which reacts rapidly with group (B) can alternatively be a compound containing two imidazolidine groups of formula (I), for example an imidazolidine of a dicarboxylic acid such as adipic or sebacic acid or an imidazolidine of a di(secondary or tertiary alcohol) such as hexane-2,5-diol or 2,5-dimethylhexane-2,5-diol or an imidazolidine of a di(primary amine) such as hexane-1,6-diamine. The imidazolidine of a dicarboxylic acid can be reacted with a tris (primary amine) such as tris(2-aminoethyl)amine to produce a hyperbranched polyamide or with a tris(primary alcohol) such as triethanolamine to produce a hyperbranched polyester. The imidazolidine of a diol can be reacted with a triol such as triethanolamine to produce a hyperbranched polycarbonate or with a primary triamine such as tris(2-aminoethyl) amine to produce a hyperbranched polyurethane. The imidazolidine of a diamine can be reacted with a primary triamine to produce a hyperbranched polyurea or with a triol to produce a hyperbranched polyurethane.

Alternatively, a compound containing three imidazolidine groups of formula (I), derived from a tricarboxylic acid or a triol such as tris(2-hydroxypropyl)amine or a triamine such as tris(2-aminoethyl)amine, can act as the polyfunctional compound having at least three functional groups (B), with for example a compound containing two primary amine or primary alcohol groups acting as the reagent which reacts rapidly with group(B). The imidazolidine of a tricarboxylic acid can be reacted with a primary diamine such as ethylene diamine to produce a hyperbranched polyamide or with a diol such as pentane-1,5-diol to produce a hyperbranched polyester. The imidazolidine of a triol can be reacted with a primary diamine to produce a hyperbranched polyurethane or with a diol to produce a hyperbranched polycarbonate. The imidazolidine of a triamine can be reacted with a diamine to produce a hyperbranched polyurea or with

- 15 -

a diol to produce a hyperbranched polyurethane.

Many of the hyperbranched polymers of the invention have reactive functional groups at the surface and are thereby suitable for use as ingredients of high-solids coatings and sealants; they can be cured through their functional groups to form solid coating films. They can also be used as reactive plasticisers in thermoplastic compositions. The hyperbranched polymers can alternatively be used as rheology modifiers in coating and sealant compositions, causing a greater reduction of viscosity than a similar amount of volatile solvent.

Hyperbranched polymers having reactive functional groups at the surface can be used to bind biological reagents such as enzymes or antigens, as described for example in US-A-5229490, providing a high concentration of the biological reagent in a low molecular volume. Alternatively, new colourants can be formed by attaching chromophores at the surface of the hyperbranched polymer.

In some uses it may be preferred to remove or reduce the number of surface functional groups. Hydroxyl groups can for example be esterified. A hydroxy-functional hyperbranched polyurethane which is water-soluble is rendered water-insoluble if most of its hydroxyl groups are esterified to benzoate groups. Similarly, amine-functional groups can be converted to amide groups to reduce water solubility. The surface functional groups can if desired be reacted with a compound containing a reactive functional group and one or more non-reactive groups which affect the properties of the polymer, for example fluoro or silicone groups to give low surface energy.

It will be seen from Figure 1 above that the hyperbranched polymer contains one group A. It is assumed that this has become unreactive with groups B due to a steric effect. This group A can be reacted with a compound

- 16 -

having two or more groups more reactive than group B to couple two or more hyperbranched polymer molecules. For example, a hyperbranched polyester containing an imidazolidine group derived from a dihydroxycarboxylic acid can be coupled by a di(primary amine).

The invention is illustrated by the following Examples:-

Example 1

A solution of N-(3-aminopropyl)-diethanolamine (3.00g, 18.5 mmol) in tetrahydrofuran (THF) (30 ml) was added dropwise to a solution of carbonyl diimidazole (3.00g, 18.5 mmol) in THF (45 ml) and stirred at room temperature for 20 hours to form an imidazolidine.

Potassium hydroxide (0.1g, 1.8 mmol) was added to the reaction mixture and the solvent removed in vacuo. The residue was then heated at 120°C for 3 hours. THF (60 ml) was added to the residue and heated at 60°C for 1 hour. The THF was decanted and the residue dried in vacuo to give a yellow gum. This was a hyperbranched urethane polymer of maximum molecular weight 6000 and number average molecular weight M_n 1075 as measured by MALDI (matrix assisted laser desorption ionisation mass spectrometry). The degree of branching was estimated at 0.6 by ^{15}N NMR.

Example 2

A solution of bishydroxymethylpropionic acid (2.00 g, 15 mmol) and carbonyl diimidazole (2.40g, 15 mmol) in THF (60 ml) was stirred at room temperature for 2 hours.

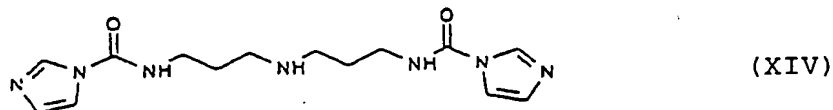
Potassium hydroxide (0.2g, 3.6 mmol) was added to the reaction mixture and the solvent removed in vacuo. The residue was then heated at 90°C for 3 hours. THF (60 ml) was added to the residue and heated at 60°C for 1 hour. The THF

- 17 -

was decanted and the residue dried in vacuo to give a colourless gum. This was a hyperbranched polyester of Mw 2426 and Mn 2421 as measured by MALDI. The degree of branching was measured as 0.49 by quantitative carbon-13 NMR; the chemical shift of the quaternary carbon atom varies according to whether it is surrounded by 3 ester units (dendritic unit), 2 ester units (linear unit) or one ester unit (terminal unit).

Example 3

10 A solution of dipropylene triamine (2.00g, 15mmol) in THF (10ml) was added to a solution of carbonyl diimidazole (4.95g, 30mmol) in THF (70ml) at 0°C and stirred at 0°C for 2 hours to form an AB₂ monomer of the formula:



15 Without isolation, the product was then reacted at room temperature for 20 hours. The reaction mixture was concentrated in vacuo to give a hyperbranched polyurea as a white sticky solid. Molecular weight was measured by MALDI and gave maximum molecular weights up to 3500.

20

Example 4

Carbonyl diimidazole (2.00g, 12mmol) was added to a solution of trisaminoethylamine (1.80g, 12mmol) in THF (100ml) at 0°C and stirred for 4 hours at 0°C and then at room temperature for 18 hours. The THF was decanted, the residue dissolved in methanol and then concentrated in vacuo to give a hyperbranched polyurea as a yellow liquid. Molecular weight was measured by MALDI and gave maximums up to 3000.

- 18 -

Example 5

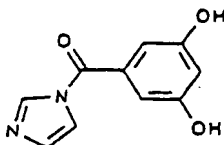
Carbonyl diimidazole (3.63g, 22mmol), trimethylolpropane (3.00g, 22mmol) and potassium hydroxide (0.2g, 3.5mmol) in THF (50ml) were heated at 60°C for 3 hours. The solvent was removed and the residue heated at 60°C for a further 3 hours to give a hyperbranched polycarbonate as a colourless gum. Molecular weight was measured by MALDI and gave maximums up to 5000.

Example 6

10 Carbonyl diimidazole (3.00g, 19mmol) was added to sebacic acid (1.87g, 9.3mmol) in methanol (50ml) and stirred at room temperature for 2 hours to form the bis(imidazolide) of sebacic acid. Trisaminoethylamine (1.35g, 9.3mmol) was added to the solution and the reaction stirred at room
15 temperature for 96 hours, then concentrated in vacuo to give a hyperbranched polyamide as a yellow liquid.

Example 7

A solution of 3,5-dihydroxybenzoic acid (2.00g, 13mmol) and carbonyl diimidazole (2.10g, 13mmol) in THF (60ml) was
20 stirred at room temperature for 2 hours to form an imidazolide of the formula:



(XV)

Potassium hydroxide (0.2g, 3.6mmol) was added to the solution and the reaction mixture stirred at room
25 temperature for 24 hours, then concentrated in vacuo. Water

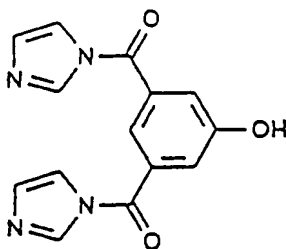
- 19 -

was added to the residue and the pale brown precipitate filtered and dried in vacuo to give a hydroxy-terminated hyperbranched polyester as a brown solid. Molecular weight was measured by MALDI and gave maximums up to 3500.

5

Example 8

A solution of 5-hydroxyisophthalic acid (1.69g, 9.3mmol) and carbonyl diimidazole (3.00g, 19mmol) in THF (60ml) was stirred at room temperature for 2 hours to form a bis(imidazolide) of the formula:



10

(XVI)

The solvent was removed and the residue heated at 90°C for 3 hours and cooled. THF was added to the residue, and the white precipitate was removed by filtration and dried in vacuo to give a hyperbranched polyester as a white solid. Molecular weight was measured by MALDI and gave maximums up to 6000. The hyperbranched polyester had terminal acid functionality as a result of hydrolysis of imidazolide groups by ambient moisture during work-up.

15

Example 9 - Synthesis of a Hyperbranched
Polyester/Polyurethane Copolymer

20

Step 1: A solution of 3-aminopropyldiethanolamine (3.00g, 19mmol) in THF (30ml) was added to a solution of carbonyl diimidazole (3.00g, 19mmol) in THF (45ml) and stirred at room temperature for 20 hours to form imidazolide (VIII).

25

- 20 -

Step 2: A solution of bishydroxymethylpropionic acid (2.48g, 19mmol) and carbonyl diimidazole (3.00g, 19mmol) in THF (60ml) was stirred at room temperature for 2 hours to form imidazolide (VII).

5 Step 3: The reaction mixtures produced in steps 1 and 2 were combined and concentrated in vacuo. The residue was heated at 90°C for 3 hours and cooled. THF (100ml) was added to the residue and heated at 60°C for 1 hour. The THF was decanted and the residue dried in vacuo to give the
10 copolymer as an orange gum.

Example 10 - Synthesis of a Hyperbranched Aliphatic Polyester/Aromatic Polyester Copolymer

Step 1: A solution of 3,5-dihydroxybenzoic acid (1.90g, 12mmol) and carbonyl diimidazole (2.00g, 12mmol) in THF
15 (60ml) was stirred at room temperature for 2 hours to form imidazolide (XV).

Step 2: A solution of bishydroxymethylpropionic acid (1.65g, 12mmol) and carbonyl diimidazole (2.00g, 12mmol) in THF (60ml) was stirred at room temperature for 2 hours to
20 form (VII).

Step 3: The reaction mixtures produced in steps 1 and 2 were combined and concentrated in vacuo. The residue was heated at 90°C for 3 hours and cooled. THF (100ml) was added to the residue and heated at 60°C for 1 hour. The THF was
25 decanted and the residue dried in vacuo to give the copolymer as a pale brown solid.

- 21 -

Example 11 - Modification of the Surface Functionality
of a Hyperbranched Polyurethane

A solution of benzoic acid (0.57g, 4.7mmol) and carbonyl diimidazole (0.76g, 4.7mmol) in THF (30ml) was stirred at room temperature for 2 hours to form the imidazolide. The imidazolide so prepared was added to the hydroxy-terminated hyperbranched polyurethane produced in Example 2 (0.76g) and potassium hydroxide (0.1g, 1.7mmol) and the reaction mixture stirred at 60°C for 5 hours. The reaction mixture was concentrated in vacuo to give the hyperbranched polyurethane terminated with benzoate ester groups. NMR analysis revealed the presence of the benzoate ester groups and the absence of any hydroxyl groups, indicating that complete reaction of all of the original 15 hydroxy groups had occurred.

Example 12 - Synthesis of a Hyperbranched Aromatic
Polyester/Polyurethane Copolymer

Step 1: A solution of 3-aminopropyldiethanolamine (3.00g, 19 mmol) in THF (30 ml) was added to a solution of carbonyl diimidazole (3.00g, 19 mmol) in THF (45 ml) and stirred at room temperature for 20 hours.

Step 2: A solution of 3, 5-dihydroxybenzoic acid (2.52g, 19 mmol) and carbonyl diimidazole (3.00 g, 19 mmol) in THF (60 ml) was stirred at room temperature for 2 hours.

Step 3: The reaction mixtures from steps 1 and 2 were combined and concentrated in vacuo. The residue was heated at 90°C for 3 hours and cooled. THF (100ml) was added to the residue and heated at 60°C for 1 hour. The THF was decanted and the residue dried in vacuo to give the copolymer as an orange gum.

- 22 -

Example 13

A solution of the biscarbonylimidazolidine of 2,5-dimethyl-2,5-hexanediol (10.00 g, 0.03 mol, prepared from 2,5-dimethyl-2,5-hexanediol and an excess of carbonyl diimidazole) and tris (aminoethyl)amine (4.37g, 0.03 mol) in 5 toluene (100 ml) was stirred at 60°C for 3 hours. The toluene was decanted while hot and the remaining gummy precipitate was washed with more toluene and dried in vacuo to give a hyperbranched polyurethane as a pale yellow gum.

10

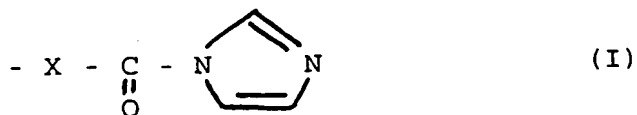
Example 14

A solution of the biscarbonylimidazolidine of 2,5-dimethyl-2,5-hexanediol (10.00g, 0.03 mol) and triethanolamine (4.47g, 0.03 mol) in toluene (100ml) was stirred at 60°C for 3 hours. The toluene was decanted while 15 hot and the remaining gummy precipitate was washed with more toluene and dried in vacuo to give a hyperbranched polycarbonate as a pale yellow gum.

- 23 -

CLAIMS

1. A process for the preparation of a hyperbranched polymer by the polymerisation of a compound containing a single group (A) of one chemical type and at least two groups (B) of a different chemical type which is reactive with (A), characterised in that the single group (A) is a group of the formula:



10 where Q represents O or S and X represents -O-, -S-, -NH- or a direct bond, the group being linked to the remainder of the compound through a carbon atom.

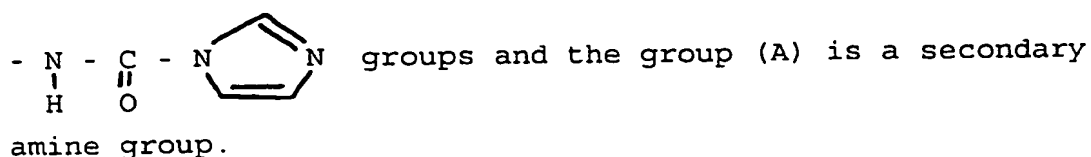
2. A process for the preparation of a hyperbranched polymer by the polymerisation of a compound containing a single group (A) of one chemical type and at least two groups (B) of a different chemical type which is reactive with (A), characterised in that either the group (A) or the group (B) is a group of the formula:



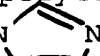
20

where Q represents O or S and X' represents -NH- or a direct bond, the group being linked to the remainder of the compound through a carbon atom.


3. A process according to claim 2, for the preparation of a hyperbranched polyurea, characterised in that the groups (B) are



- 24 -

4. A process according to claim 2, for the preparation of a hyperbranched polyester, characterised in that the group (II) is a - C(=O) - N  N group

5 and the other group (A) or (B) is a hydroxyl group.

5. A process according to claim 2, for the preparation of a hyperbranched polyurethane, characterised in that the group (II) is a - N(H) - C(=O) - N  N group

10 and the other group (A) or (B) is a primary or secondary alcohol group.

6. A process for the preparation of a hyperbranched polymer by the polymerisation of a compound containing a single group (A) of one chemical type and at least two
15 groups (B) of a different chemical type which is reactive with (A), characterised in that a precursor compound, containing either a single group (A') of one chemical type reactive with carbonyl diimidazole and at least two groups (B) of a different chemical type from A' which is less
20 reactive than A' with carbonyl diimidazole or at least two groups (B') of one chemical type reactive with carbonyl diimidazole and a single group (A) of a different chemical type from B' which is less reactive than B' with carbonyl diimidazole, is reacted with carbonyl diimidazole under
25 conditions such that only the group A' or the groups B' react with the carbonyl diimidazole to form imidazolide groups, and the resulting compound containing imidazolide groups is polymerised under more vigorous reaction conditions to form the hyperbranched polymer.

30 7. A process according to claim 6, for the preparation of a hyperbranched polyester, characterised in that the group A' or groups B' of the precursor compound are carboxylic acid groups and the groups B or A respectively of the precursor compound are hydroxyl groups, and the more
35 vigorous reaction conditions comprise heating or catalysis

-25-

by a basic catalyst.

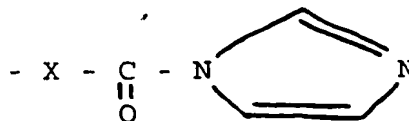
8. A process according to claim 6, for the preparation of a hyperbranched polyurethane, characterised in that the group A' or groups B' of the precursor compound 5 are primary amine groups and the groups B or A respectively of the precursor compound are primary or secondary alcohol groups, and the more vigorous reaction conditions comprise heating or catalysis by a basic catalyst.

9. A process according to claim 6, for the preparation of a hyperbranched polyurea, characterised in that the precursor compound is a diprimary secondary amine and is reacted with carbonyl diimidazole at 0°C or below, and the more vigorous reaction conditions comprise a higher temperature which is ambient temperature or above.

10. A process for the preparation of a hyperbranched polymer, characterised in that a polyfunctional compound having at least three reactive functional groups (B) is reacted in substantially equimolar quantities with a reagent which reacts rapidly with group (B) to form a group (A) which reacts more slowly with group (B) than the reagent does.

11. A process according to claim 10, characterised in that the reagent is carbonyl diimidazole and the groups (B) are primary amine or primary alcohol groups.

12. A process according to claim 10, characterised in that the reagent is an imidazolide containing two groups of the formula:-



where Q represents O or S and X represents -O-, -S-, -NH- or a direct bond, the group being linked to the

- 26 -

remainder of the compound through a carbon atom, and the polyfunctional compound is a tris(primary amine) or a tris(primary alcohol).

13. A process according to claim 10, characterised in that the said polyfunctional compound is an imidazolidine containing three groups of the formula (I) as defined in claim 3 and the reagent is a compound containing two primary amine or primary alcohol groups.

14. A hyperbranched polymer characterised in that all or most of the chemical linkages in the polymer are urea linkages.

15. A process for the preparation of a hyperbranched polymer by the polymerisation of a compound containing a single group (A) of one chemical type and at least two groups (B) of a different chemical type which is reactive with (A), characterised in that either the group (A) or the group (B) is a group of formula (I) as defined in claim 6 and in that a hyperbranched copolymer is formed by polymerising together at least two such compounds.

16. A process according to claim 15, characterised in that the groups of formula (I) in one of the said two compounds are different from the groups of formula (I) in the other compound.

17. A process according to claim 15, characterised in that one of the said two compounds is an aromatic compound and the other is an aliphatic compound.

18. A hyperbranched polymer formed by the polymerisation of at least one compound containing a single group (A) of one chemical type and at least two groups (B) of a different chemical type which is reactive with (A), characterised in that the hyperbranched polymer is a copolymer containing two different chemical linkages, one of

- 27 -

:
- said linkages being selected from urea, urethane and carbonate linkages and the other of said linkages being selected from urea, urethane, carbonate, ester and amine linkages.

INTERNATIONAL SEARCH REPORT

national Application No

PCT/GB 98/01276

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G83/00

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BOLTON D H ET AL: "SYNTHESIS AND CHARACTERIZATION OF HYPERBRANCHED POLYCARBONATES" MACROMOLECULES, vol. 30, no. 7, 7 April 1997, pages 1890-1896, XP000684813 cited in the application see the whole document	2
P, X	GB 2 308 363 A (COURTAULDS COATINGS) 25 June 1997 see claims 1,6-9	18

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

10 August 1998

Date of mailing of the international search report

18/08/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Niaounakis, M

Information on patent family members

PCT/GB 98/01276

Form PCT/ISA/210 (patent family annex) (July 1992)